THE REDUCTION OF NITROGLYCERIN WITH TITANOUS SULPHATE

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Abstract

A study of the reduction of nitroglycerin with titanous sulphate has been carried out. The results indicate that for each mole of nitroglycerin reduced, 18 moles of titanous ion are oxidized, two moles of ammonia, one-half mole of nitrogen trioxide, and one mole of glycerol are formed. It has been shown that the reduction takes place first to 1,3-dinitro-2-nitrosoglycerin which, after hydrolysis to 1, 3-dinitroglycerin, is reduced to glycerol with the probable intermediate formation of 1, 3-dinitrosoglycerin. The determination of nitroglycerin by the Shankster and Wilde method is more accurate when 70% acetic acid is substituted for methanol as the solvent for nitroglycerin.

It was found by Oldham (5) that in the reduction of nitric esters with titanous chloride, each mole of the ester consumed 7.5 moles of titanous ion. If the reduction were to go to completion, then eight moles of the titanous chloride would be consumed as shown by Equation (1).

The reduction of nitroglycerin, if carried through to completion, might therefore be expected to correspond with the following equation:

Shankster and Wilde (6) showed, however, that only 18 moles of titanous chloride are consumed quantitatively by one mole of nitroglycerin, and postulated, but did not investigate, the following equation:

In carrying out the Shankster and Wilde procedure, which consists of refluxing a methanolic solution of nitroglycerin with excess titanous sulphate followed by back-titration of the excess titanous sulphate with standard ferric alum, low and inconsistent results were obtained (Table I).

During the war it was reported that a modification of the Shankster and Wilde procedure yielded complete reduction of the nitroglycerin to ammonia,

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TABLE I

THE REDUCTION OF NITROGLYCERIN (SHANKSTER AND WILDE METHOD)

Wt. of nitroglycerin added, mgm.	Wt. of nitroglycerin found, mgm.*	% Recovery
27.77	21.94	79.0
10.73	9.37	87.3
10.73	10.07	93.9

* Based on 1 mole nitroglycerin = 18 gm. atom Ti^{+++}

giving an equivalence of 24 moles of titanous salt per mole of nitroglycerin in accordance with Equation (2). This modification consisted of substituting 70% acetic acid for methanol as the solvent for nitroglycerin and the use of phosphorus-free titanous chloride. Phosphorus-free titanous chloride was employed as it was found that the presence of this element interfered in the reduction.

Attempts to repeat this result were unsuccessful (Table II), it being found that 18 instead of 24 moles of titanous ion were consumed by each mole of nitroglycerin. However, as can be seen from the results, considerably better precision and accuracy are obtainable with the modified method than with the original.

TABLE II

THE REDUCTION OF NITROGLYCERIN (MODIFIED METHOD)

Wt. of nitroglycerin added, mgm.	Wt. of nitroglycerin found, mgm.*	% Recovery
21.38	21.37	99.96
21.38	21.36	99.95
20.30	20.38	100.4
20.30	20.44	100.7
20.30	20.32	100.1
20.30	20.18	99.40
20.30	20.24	99.70
20.30	20.12	99.10
20.59	20.39	99.27
Average.....		99.88%
Mean deviation.....		$\pm 0.42\%$

* Based on 1 mole nitroglycerin = 18 gm. atom Ti^{+++}

In an endeavor to account for the higher equivalence found by the original workers using the modified method, the possible catalytic effects of iron and aluminum known to be present in the titanous solutions used by them were studied. As can be seen from Table III, no significant effect was observable in these experiments.

Attention was then turned to variation of acidity as a possible cause of difference between the results of the various workers. Table IV shows that increase in acidity brings about a decrease in the amount of titanous ion con-

TABLE III

EFFECT OF IRON AND ALUMINUM ON THE MODIFIED METHOD

Reagent added	Nitroglycerin added, mgm.	Nitroglycerin found, mgm.*	% Nitroglycerin found
10 ml. 0.25 <i>M</i> AlCl ₃	23.18	23.16	99.92
10 ml. 0.25 <i>M</i> AlCl ₃ +			
10 ml. 0.1 <i>M</i> ferric alum	23.18	23.22	100.2
10 ml. 0.1 <i>M</i> ferric alum	23.18	23.16	99.92

* Based on 1 mole nitroglycerin = 18 gm. atom Ti⁺⁺⁺

TABLE IV

EFFECT OF ACIDITY ON THE MODIFIED METHOD

Ml. H ₂ SO ₄ added	Ml. titanous sulphate used	Millimoles titanous sulphate used	Millimoles nitroglycerin present	Moles titanous sulphate consumed per mole nitroglycerin reduced
0.56	9.58	1.695	0.09414	18.01
5	6.94	1.228	"	13.04
20	5.32	0.9411	"	9.99
40	4.85	0.8572	"	9.11
80	4.80	0.8493	"	9.02

N titanous sulphate = 0.1769.

sumed. The results, moreover, tend to a minimum corresponding with an equivalence of nine moles of titanous salt per mole of nitroglycerin (Table IV).

The minimum value reached corresponds to the equation

which could occur if the reduction is preceded by hydrolysis of the ester.

Since the earlier experiments had shown a consumption of 18 equivalents of titanous salt per mole of nitroglycerin, it is unlikely under the reaction conditions then used that the formation of nitric acid or nitrate ion precedes the reduction. This introduces the possibility of differences in the reactions undergone respectively by the primary and secondary nitric ester groups present in nitroglycerin. To throw further light on this, a detailed study of the reaction was undertaken.

Behavior of the Primary Nitrate Group

To verify that polyfunctional aliphatic primary nitric esters are reduced to ammonia and the corresponding alcohols, solutions of pentaerythritol tetranitrate and methyltrimethylolmethane trinitrate (containing 4 and 5 primary nitrate groups respectively) were refluxed with titanous sulphate. It was found that these compounds are reduced to the extent of about 90% to ammonia and the corresponding alcohols with no formation of nitrogen trioxide.

It was thought probable that the reduction of the primary nitric ester groups of nitroglycerin to ammonia takes place with the intermediate formation of 1,3-dinitrosoglycerin. If such is the case, then primary nitrites should be reduced by titanous sulphate to ammonia. This was verified by refluxing *n*-butyl nitrite with titanous sulphate and analyzing the reaction products.

It was found that ammonia was formed, titanous sulphate was oxidized, and no oxides of nitrogen were evolved.

Behavior of the Secondary Nitrate Group

Analysis of the gaseous products (Table V) formed in the reduction of nitroglycerin with titanous sulphate shows that for each mole of nitroglycerin reduced, two moles of ammonia and one-half mole of nitrogen trioxide are formed,

TABLE V
DETERMINATION OF GASEOUS REACTION PRODUCTS

Wt. of nitro- glycerin, mgm.	Wt. of ammonia recovered, mgm.	Molar ratio ammonia/ nitroglycerin	Wt. of nitrogen trioxide re- covered, gm.	Molar ratio nitrogen trioxide/ nitroglycerin
32.07	4.81	2.00	0.0163	0.455
32.07	4.72	1.96	0.0923	0.500
		Av. 1.98		Av. 0.48

suggesting that two of the nitrate groups are completely reduced and the third only partially, forming 1,3-dinitro-2-nitrosoglycerin as an intermediate. It is not unreasonable to assume then that the reduction is symmetrical in that the two moles of ammonia formed are derived from the two primary nitrate groups which are equivalent to each other, the nitrogen trioxide being formed through the partial reduction of the secondary nitrate group, followed by hydrolysis without further reduction. If such is the case, then it would be expected that the reaction is a stepwise one. Indeed, the potentiometric titration of nitroglycerin with titanous sulphate bears this out (Fig. 1).

It may be calculated from the data given in Fig. 1 that the first inflection in the curve takes place at the point where just enough titanous sulphate has been added to reduce one nitrate group to the nitroso stage. Since this reduction is only a partial one, it appears to be the secondary nitrate group which is thus affected since it has already been shown that the primary nitrate groups in nitroglycerin are completely reduced.

FIG. 1. The potentiometric titration of nitroglycerin with titanous sulphate.

To show that the intermediate compound 1, 3-dinitro-2-nitrosoglycerin may be hydrolyzed, without further reduction, in the presence of titanous sulphate, secondary butyl nitrite was prepared (4) and refluxed with titanous sulphate. There occurred an immediate evolution of a gas which, when analyzed, was shown to be nitrogen trioxide. Titration of the solution with standard ferric alum showed no oxidation of the titanous salt. Analysis of the reaction products showed no evidence of ammonia formation.

We may therefore conclude on the basis of the above evidence that the nitrogen trioxide formed during the reduction of nitroglycerin comes from the secondary nitrate group, through hydrolysis of the intermediate nitroso compound (Equation (6)).

Isolation of 1, 3-Dinitroglycerin

1, 3-Dinitroglycerin was isolated from the reaction mixture and yielded a benzoyl derivative melting at 67–68°C. and a *p*-nitro benzoyl derivative melting at 94–95°C. These melting points correspond to those given by Will (7) for the benzoyl and *p*-nitrobenzoyl derivatives of 1, 3-dinitroglycerin.

The reduction of nitroglycerin with titanous sulphate may now be formulated as follows:

Experimental

Materials

1. Pure titanous sulphate in 1*N* sulphuric acid prepared by dissolving pure titanium hydride in 145 ml. of warm 35% sulphuric acid. The resulting solution after filtration was diluted to one liter with freshly boiled distilled water and stored under an atmosphere of carbon dioxide.

2. A standard solution of nitroglycerin in 70% acetic acid (about 0.2%), prepared by weighing out a definite amount of nitroglycerin into a tared stoppered weighing bottle and transferring quantitatively into a volumetric flask.

3. Standard solutions of: ferrous ammonium sulphate; ferric ammonium sulphate; potassium permanganate; hydrochloric acid.

4. 5% Ammonium thiocyanate; 40% sodium hydroxide; 5% nitric acid in 95% sulphuric acid.

5. Milligan gas washing bottles; Beckman Model H-2 pH meter equipped with a platinum and tungsten electrode.

Modified Method

A 10 ml. aliquot of the standard nitroglycerin solution was pipetted into an Erlenmeyer flask equipped with a side arm, and the air expelled by a stream of carbon dioxide which was maintained throughout the determination. Twenty milliliters of 0.2 *N* titanous sulphate was then added from a carbon dioxide filled burette. The contents was boiled under reflux for 10 min., cooled to room temperature, and the excess titanous sulphate titrated with standard 0.15*N* ferric ammonium sulphate, 5 ml. of 5% ammonium thiocyanate being added toward the end of the titration as indicator.

A blank determination using 10 ml. of 70% acetic acid in place of the nitroglycerin solution was carried on simultaneously. The difference between the two titrations gave the titanous sulphate consumed by the nitroglycerin.

This method differs from that of Shankster and Wilde (6), mainly in the use of 70% acetic acid instead of methanol as a solvent for nitroglycerin.

Effect of Acidity

The modified method was employed except that varying amounts of acid were added before reflux was begun. The practice was adopted of diluting to a final normality of not more than 5*N* with respect to sulphuric acid (in the case of the concentrated acid solutions) since the end point was unsatisfactory at higher concentrations.

Determination of Ammonia

After reduction of the nitroglycerin, enough 40% sodium hydroxide was added to the cold solution both to precipitate the titanium salts and to make the solution alkaline. The ammonia formed was distilled from the solution into boric acid and determined by titration with standard hydrochloric acid.

Determination of Nitrogen Trioxide

The basic method employed is that of Milligan (3). A stream of carbon dioxide (source—dry-ice) was bubbled through the boiling reaction mixture into a train of two Milligan gas washing bottles. The first bottle (*A*) contained 200 ml. of 95% sulphuric acid for the absorption of nitrogen dioxide, and the second bottle (*B*) contained 200 ml. of a 5% solution of nitric acid in 95% sulphuric acid for the absorption of nitric oxide. Carbon dioxide was swept through the apparatus for a period of two hours, after which time a 25 ml. aliquot was removed from each bottle, and added, with cooling, to 800 ml. of diluted potassium permanganate (containing 10 ml. of phosphoric acid to prevent the precipitation of oxides of manganese). An excess of standard ferrous sulphate was then added, the excess being back-titrated with the standard permanganate.

Results in Table V indicate that the gas formed from the reduction of one mole of nitroglycerin consists of one-half mole of nitrogen trioxide (or of an equimolar mixture of nitric oxide and nitrogen dioxide).

According to Lunge and Berl (1, 2), the absorption of an equimolecular mixture of nitric oxide and nitrogen dioxide is practically complete in concentrated sulphuric acid, two moles of nitrosylsulphuric acid being formed as shown by the following equations:

Since there was no gas absorbed in bottle (B), nitric oxide alone was not evolved.

When nitrogen dioxide alone is absorbed in sulphuric acid, only one mole of nitrosylsulphuric acid is formed for each two moles of nitrogen dioxide.

The results obtained from the analysis of the gases absorbed in bottle (A) (Table V) clearly indicate that nitrogen dioxide alone was not evolved since one mole of nitrosylsulphuric acid was formed per mole of nitroglycerin reduced, and it had already been shown that two of the three nitrogen atoms in nitroglycerin were reduced to ammonia.

Potentiometric Titration of Nitroglycerin with Titanous Sulphate

To 50 ml. of 70% acetic acid containing 0.275 gm. of nitroglycerin was added 150 ml. of 30% sodium acetate. After each addition of 1 ml. of 0.2N titanous sulphate, the solution was allowed to react for five minutes before measurements of the e.m.f. were taken. Throughout the titration the solution was kept at 95°C. and at constant volume in an atmosphere of carbon dioxide. The results obtained are plotted in Fig. 1.

Isolation of 1, 3-Dinitroglycerin

To a solution of nitroglycerin in acetic acid was added just enough titanous sulphate to reduce the secondary nitrate group to the nitrite. The solution was refluxed and after the reaction was complete, the mixture was cooled, filtered free from hydrated titanous oxide, and extracted with ether. A yellow oil obtained after evaporation of the ether yielded a benzoyl derivative melting at 67–68°C. and a *p*-nitrobenzoyl derivative melting at 94–95°C.

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